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EBULLIOSCOPIC MEASUREMENTS IN MIXED LIQUIDS

By

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A Thesis

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EBULLIOSCOPIC MEASUREMENTS IN MIXED LIQUIDS

The study of the variation of some physical property with the composition of a binary mixture has been carried on for a long time as a means of securing an experimental basis for a theory of mixtures. The properties which have been studied are numerous including viscosity, boiling points, refractive indices, densities, specific volumes, and various thermal properties. Poisseule in 1843 and 1847 published papers on the viscosity of mixtures particularly those of ethyl alcohol and water. About the same time Bineau found that the constant boiling mixture of hydrochloric acid and water had approximately the composition $HCl\cdot 8H_2O$ and the similar mixture of nitric acid and water was represented as $2HNO_3\cdot 3H_2O$. This work resulted in the hypothesis that these constant boiling mixtures are definite chemical compounds. That hypothesis has since been shown to be untenable since Roscoe and Dithmar and others have found that the composition of the constant boiling mixture depends on the pressure and in the case of mixtures of ethyl alcohol and water it has been found that at low pressures the minimum in the boiling point curve disappears. Such mixtures are therefore not considered definite compounds any more but the existence of a maximum or minimum in a boiling point curve is taken as evidence of either a certain amount of combination or a change in the association

or dissociation of the liquids composing the mixture. The argument which applies to boiling points has been found to apply also to other properties such as viscosity and heats of mixture.

The thermodynamic treatment of mixtures began with the work of Kirchhoff[1] and Gibbs[2] on the vapor pressure of liquid mixtures. The theory advanced by Gibbs was worked out independently on an experimental basis by Konowalow[3]. He distinguished three types of vapor pressure curves for completely miscible liquids and studied the changes occurring in the distillation of mixtures. The work of Kirchhoff was extended by Duhem[4] who deduced a differential equation for the change of the logarithm of the vapor pressure with the composition of the mixture. This equation was later integrated by Margules[5] and confirmed quantitatively by v.Zawidzki[6]. Others have studied various special problems in the thermodynamic theory of mixtures and in some cases experimental confirmation has been secured[7]. The general theory of binary systems has been attacked by Gibbs[8], Planck[9] and Duhem[10] who

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1. Kirchhoff. Pogg. Ann. 103 104 (1858).
2. Gibbs. Scientific Papers Vol. I.
3. Konowalow. Wied. Ann. 4 48 (1881).
4. Duhem. Traite de Mecanique Chemique IV.
5. Margules. Sitzungsber. Wien. Akad. 1895.
6. Zawidzki Z. physikal. chem. 35 129 (1900).
7. Nernst Theoretische Chemie 6th Ed. P.115. Bose Z.physikal chem. 58 621 (1907), ibid. 65 458 (1909) van der Waals Proc. Acad. Amsterdam 10 56,123,183 (1909).
8. Gibbs Scientific Papers B Vol. I.
9. Planck Thermodynamik 3 Aufl. Sec. 211.
10. Duhem. Traite I ch.viii III ch. i,ii.

have derived a general equation for the displacement of equilibrium of a system. This equation has been applied in a few cases and Masing[11] has applied it ot the calculation of the heats of vaporization of water and ethyl alcohol and mixtures of the two. In general, however, this equation and the others have approximations introduced so as to put them into a form which may be used in calculations so that the calculated results do not agree as well as might be hoped for.

Leaving, for the time being, the purely thermodynamic theory of mixtures we have the work of Dolezalek[12] advocating the chemical theory of mixtures. He started with the assumption that the partial pressure of each component is proportional to its concentration in the liquid phase provided no chemical change occurs on mixing the liquids and that neither one is polymerized in the liquid state. If there is any association of either component the partial pressure curve of that component is concave to the concentration axis indicating dissociation of the polymerized molecules. If the curve is concave the other way, the formation of a compound of the two components is indicated. On this basis Dolezalek discussed the pairs benzene-chloroform, carbon tetrachloride-benzene, and chloroform-acetone. In the case of the chloroform-acetone mixtures by using the assumption

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11. Masing Z.physikal. chem. 81 223 (1912).
12. Dolezalek Z.physikal. chem. 64 727 (1908). 71 191 (1910). 83 40,45 (1913).

already stated and applying the mass law to the reaction between the two components he succeeded in calculating the partial pressures of the chloroform and acetone at 35° C. obtaining results in good agreement with those obtained experimentally by v. Zawidzki. He also calculated the amount of combination that took place in the mixture finding a maximum of 18 per cent conbined molecules in a mixture containing equimolar quantities of the chloroform and acetone. In the case of the carbon tetrachloride-benzene mixture he was able to calculate the amount of association of the carbon tetrachloride, finding 15 per cent double molecules at 50° C. The theory of Dolezalek was attacked by van Laar[13] and Patterson[14], who proposed a theory based largely on kinetic considerations. The fact remains, however, that Dolezalek's[15] treatment of the mixture ether-chloroform furnishes considerable experimental basis for his theory and shows that this theory is one which is well worth investigating further.

It will be noted that the theoretical work referred to thus far has been based on the study of vapor pressures as might be expected since these lend themselves most readily to thermodynamic treatment. The work based on other properties of mixtures has resulted in a large number of more or less empirical equations which fit some cases but fall far short

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13. van Laar Z.physikal. chem. 72 723 (1910).
14. Patterson ibid. 68 572 (1909).
15. Dolezalek ibid. 83 40, 45 (1913).

of the requirements in others. It was with the hope of securing an experimental basis for an investigation of the theory of mixtures that the present work, on the elevation of the boiling point of a binary mixture on the addition of a third substance which was non-volatile, was taken up. The first work of this kind was done by Haverstick[16] on mixtures of methyl and ethyl alcohol using benzoic acid as the third substance. The apparatus used by Haverstick was improved and the work continued by Carroll[17], who worked with the pairs ether-acetone, benzene-ethyl alcohol, carbon tetrachloride- ethyl acetate. The present work on the pairs chloroform-acetone and ethyl alcohol - water was then started. The pair chloroform - acetone was selected since it is one case in which a definite compound can be isolated and therefore ought to serve as a means of testing this method of detecting compounds in liquid mixtures. The other pair, alcohol - water was selected because there has been so much work done on such mixtures that there is a great deal of data available for correlation with any new data that may be brought forth. The solutes selected, camphor for the chloroform - acetone mixtures and acetamide for the alcohol - water, are such that the rise in boiling point of each liquid is directly

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[16] University of Wisconsin. Thesis. 1916.
[17] Work started in 1919 and is still in progress.

proportional to the amount of acetamide added. It may be mentioned in this connection also that in no case has it been found that a solute which obeyed this linear relation in each of the pure liquids did not obey it in all mixtures of the two.

Let us review briefly the previous work on these pairs of liquids.

Cameron and Holly[18] isolated a compound from a mixture of acetone and chloroform containing equal molar quantities of the two substances.

Von Zawidzki[19] studied the vapor pressure relations of chloroform-acetone mixtures as has already been mentioned in connection with the theoretical work of Dolezalek.

Whatmough[20] studied the surface tensions of mixtures of chloroform and acetone and found that the surface tension was nearly a linear function of the composition.

Tsakalotos[21] studied the viscosity of mixtures of chloroform and acetone and found that the observed values were greater than those calculated by the mixture rule. He attributes this deviation to a reaction between the two components.

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[18] J. phys. chem. 2 322 (1898).
[19] loc. cit.
[20] Z. physikal. chem. 39 129 (1901).
[21] Bull. Soc. Chim. (4) 3 234,242 (1908).

Faust[22] also studied the viscosity of this system determining the isotherms at -13, 0, 19, and 39 degrees Centigrade and found that the maximum in the curve was less pronounced at the higher temperatures as might be expected if it were due to a reaction between the components which could be reversed by raising the temperature.

Findlay[23] studied the viscosity of the mixtures at their boiling points and found that the maximum deviation of the viscosity from that calculated by the mixture rule came at 80 per cent chloroform and the deviation amounted to 12 per cent.

Haywood[24] found a maximum in the boiling point curve at 80 per cent chloroform.

Holmes[25] found the maximum volume change on mixing to be at 50 volumes of acetone to 100 volumes of chloroform which is about 80 per cent chloroform by weight.

Rosanoff[26] studied the vapor pressure of mixtures of chloroform and acetone.

Beckmann and Faust[27] have determined the partial pressures of acetone and chloroform over their mixtures at different temperatures. They also studied mixtures containing

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22. Z. physikal. chem. 79 97 (1912).
23. Ibid. 69 203 (1909).
24. J. phys. chem. 3 318 (1899).
25. J. Chem. Soc. 103 2147 (1913).
26. J. Am. Chem. Soc. 36 1993 (1914).
27. Z. physikal. chem. 89 235 (1915).

a small amount of acetone at low temperatures and found that even at -65° C. combination took place immediately on mixing.

Schulze[28] has studied the vapor pressures of the mixtures and following the example of Dolezalek, he has calculated the composition of the mixtures at 30, 70, and 90 degrees Centigrade. He also gives a curve showing the effect of temperature on the equilibrium constant for the reaction between chloroform and acetone.

The mixtures of ethyl alcohol and water have been studied in much greater detail than chloroform - acetone. Doroshevskii[29] and Andrews[30] have studied the refractive index curve for the mixtures and find a maximum at 79.3 per cent alcohol at 25° C. corresponding to three molecules of alcohol to two of water. Holmes[31] also studied the refractive index curve and found the maximum deviation from the simple rule of mixtures at 79.2 per cent alcohol. He also observed the maximum volume change at the same point.

Schwers[32] reports a maximum contraction for a mixture containing 46 per cent alcohol.

The viscosity of alcohol - water mixtures has been

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[28] Ibid. 93 368 (1919).

[29] J. Russ. Phys. Chem. Soc. 40 101 See also C.P. 2 2181.

[30] J. Am. Chem. Soc. 30 353 (1908).

[31] loc. cit.

[32] Rec. trav. chim. 28 261.

studied very thoroughly. The first investigators were Poisseule[33] and Graham[34], who observed a maximum viscosity at three molecules of water to one of alcohol. Varenne and Godefroy[35] found breaks in the viscosity isotherm at points corresponding to $3H_2O \cdot 1\ EtOH$; $2H_2O \cdot 1EtOH$; $6H_2O \cdot 1EtOH$; $3H_2O \cdot 2EtOH$; $22H_2O \cdot 1\ EtOH$. Dunstan[36] reported a very pronounced maximum in the viscosity at $3H_2O \cdot 1EtOH$ and other breaks at $2H_2O \cdot 1EtOH$; $4\text{-}5\ H_2O \cdot 1\ EtOH$; $6H_2O \cdot 1EtOH$ and an indication of a break at about 3 per cent alcohol.

The boiling point curve for mixtures of alcohol and water has been investigated by Evans[37], Haywood[38], Noyes[39] and others[40] and has been found to have a minimum at about 96 per cent alcohol under atmospheric pressure. Wade amd Merriman[41] have studied the change of the location of the minimum boiling point with the pressure and have found that at pressures below 150 millimeters there is no minimum.

Vrevskii[42] studied the change in composition of the

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33. Compt. rend. 15 1167 (1843).
34. Phil. Trans. 151 373 (1861).
35. Compt. rend. --- 993 (1903).
36. J. Chem. Soc. 85 817 (1909).
37. J. Ind. Eng. Chem. 8 260-2 (1916).
38. J. phys. chem. 3 318 (1899).
39. J. Am. Chem. Soc. 23 463 (1901).
40. Ibid. 18 1063, Trans. Roy. Soc. London (1869) 591.
41. J. Chem. Soc. 99 997 (1911).
42. J. Russ. Phys. Chem. Soc. 42 1349 (1910).

mixture having a maximum vapor pressure and found that it contained 98 per cent alcohol at 39.78°, 97 per cent at 54.81° and 96.3 per cent at 74.79°.

Foote and Scholes[43] studied the composition of the vapor in equilibrium with various mixtures of alcohol and water at 25° C.

Brown[44] has studied the change in the specific volume of alcohol on dilution and found that there is a nimimum at a density 0.9652 corresponding to 24.83 per cent alcohol by weight while a hydrate of the composition EtOH - $8H_2O$ would contain 24.21 per cent.

Denison[45] has studied property-composition curves and has pointed out that the point of maximum deviation is of greater importance than the maximum value of the property. For alcohol and water he reports a maximum contraction and maximum deviation in viscosity at 46 per cent alcohol corresponding to EtOH - $3H_2O$.

Bose[46] has studied the specific heats and heats of mixture of alcohol and water. The specific heats of the mixtures were determined over the ranges 0.5 to 5.0°, 20.1 to 26.0°, 39.0 to 42.5°.

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[43] J. Am. Chem. Soc. 33 1309 (1911).
[44] Analyst 40 379 (1915).
[45] Trans. Faraday Soc. 8 20 (1915).
[46] Z. physikal. chem. 58 585 (1907).

The heats of mixture were determined at 0, 17.33, 42.04 and 74.0 degrees C. At the lower temperatures there is a large positive heat of mixing having a maximum at about one molecule of alcohol to four of water. The heat of mixing decreases with rise in temperature until at 74.0° it is positive from 0 to 22 molecular per cent alcohol and negative for all other mixtures, the maximum negative heat effect being at about 80 molecular per cent alcohol.

The surface tension of mixtures of alcohol and water have been determined by Morgan and Neidle[47] by the drop weight method, by Grunmach[48] by the capillary wave method and by Weinstein[49] by the capillary rise method. Although the absolute magnitude of the tensions as determined by the three methods differ somewhat, the shape of the surface tension - composition curve is the same. In every case this curve falls off rapidly on the addition of water reaching a maximum deviation from a linear relationship at about 25 per cent alcohol.

Masing[50] has applied Planck's general equation for the displacement of an equilibrium to the calculation of the heats of vaporization of alcohol and water and a fifty-fifty

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47. J. Am. Chem. Soc. 35 1856 (1913).
48. Ann. der phys. 38 1018 (1912).
49. Metronomische Beitrage Nr. 6 Berlin(1889).
50. Z. physikal chem. 81 223 (1912).

mixture of the two. The values calculated for the pure liquids are in good agreement with those observed experimentally but the value for the fifty-fifty mixture is too high when compared with that calculated by the rule of mixtures.

Experimental Work

Purification of Materials.

Chloroform. - Merck's U.S.P. chloroform, containing about three-fourths of one per cent of alcohol, was washed three times with an equal volume of water, then with concentrated sulphuric acid for about one hour mixing being secured by a high-speed screw stirrer in both layers. The acid showed only a slight yellow coloration after this treatment. The chloroform was then washed with water, dilute sodium carbonate solution and again with water and dried with two portions of potassium carbonate, the second portion being freshly ignited. After this the chloroform was allowed to stand for thirty hours with phosphorus pentoxide and then fractionated over some more phosphorus pentoxide at 760 mm. pressure. The distillation started at 60.7° less than one-fourth coming over below 61.0°. About two-thirds of the liquid came over between 61.0° and 61.3° and nine-tenths came over below 61.4°. Further fractionation gave a product boiling at 61.09° at 760 mm. pressure. B.p. 61.1° C.

Acetone. - Mallinckrodt's U.S.P. acetone was dried with calcium chloride from one to seven days and then distilled. The fraction distilling between 56.1° and 56.7° at 760 mm. was refluxed with sodium iodide which had been dried at 130-150° C. The saturated solution was cooled to -5 or 10

degrees C., the crystals drained and the acetone distilled off, the distillation being stopped as soon as the temperature began to rise. The distillate was then dried with metallic calcium and fractionated in the constant pressure still.[51] The portion distilling between 56.01 and 56.10 was taken, b.p. according to Timmerman's[52] 56.1° C.

Alcohol. - The commercial 95 per cent alcohol was dehydrated by allowing to stand with calcium oxide for a week, refluxing for three hours, and then distilling. The distillate was further dehydrated by refluxing with metallic calcium and distilling. This distillate was fractionated and the intermediate portions treated with metallic sodium and fractionated, the portion distilling between 78.25° and 78.35° being taken. The product thus obtained showed no coloration when a crystal of potassium permanganate was added and gave no test for aldehyde with Caro's reagent, b.p. according to Noyes 78.300.

Water. - The water used was conductivity water obtained from a still of the type which has been described by Clevenger.[53]

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51. Mathews and Faville J. phys. chem. (1917).
52. Bull. Soc. Belg. 24 244 (1910).
53. Clevenger J. Ind. Eng. Chem. 11 964 (1919)

Camphor. - A good grade of camphor was purified by two sublimations.

Acetamide. - Merck's acetamide was recrystallized from benzene three times and washed with ether and dried under reduced pressure. The product thus obtained was practically odorless and melted at 82.1° C. corrected.

Methods of Analysis.

In analyzing the samples drawn from the boiling solutions, the following methods were used:

Acetamide. - The sample was heated under a reflux condenser for half an hour with 20 cc. of approximately 1.5 N sulphuric acid. The solution was then made strongly alkaline with sodium hydroxide and the ammonia set free distilled off into 0.25 N sulphuric acid. The excess acid was titrated with carbonate free alkali using methyl red as an indicator.

Camphor.-- The camphor was determined by diluting the sample with alcohol to such a volume that it just filled a two-decimeter polarimeter tube and determining the rotation of the plane of polarization of polarized light of wave length 5461 Angstroms. The measurements were made by means of a Schmidt and Haensch polarimeter reading to one-thousandth of a degree and using as a source of light a mercury arc with the Wratten filter made to let through the green line of mercury.

Having obtained the rotation due to the sample, the concentration was read from a curve which had been made up from a series of readings on solutions of known concentration. The value thus obtained had to have a small correction applied on account of the chloroform present, but no correction was necessary on account of the acetone. The correction for the chloroform amounted to 0.02° per gram of chloroform.

Description of Apparatus.

The apparatus for determining the molecular elevations of the boiling point consisted of a boiling tube attached to a device for keeping the pressure constant at 760 mm. which permitted greater accuracy in the determinations than has been previously attained. In the determination of the boiling points, all the heating was done by a coil of platinum black and immersed in the liquid to be boiled. A current of from 9 to 12 amperes was supplied to this wire by a transformer which stepped down a sixty-cycle 110-volt circuit to 11 volts. Temperature readings were taken on a Beckmann thermometer, which could be read to a thousandth of a degree with the aid of a magnifying glass. A buzzer was attached to the stem of the thermometer so that the mercury thread could be jarred loose from the walls of the capillary in case there was any tendency for it to stick. The side tube S consisted of 1 mm. capillary tubing and was used to sample

the boiling liquid at the conclusion of a run. The reflux condenser B returned the condensed liquid to the boiling tube.

The remainder of the apparatus served as a pressure regulator to keep the pressure constant at 760 mm. in the boiling tube. The essential part of this is the diaphragm regulator G (designed by B. H. Carroll). The diaphragm was made of thin spring steel with a small piece of platinum soldered on so as to give a contact surface of non-corroding material. The other contact was a heavy platinum wire with a sharp point which was soldered to a rod which passed through a brass plug in the top of the regulator. Both the rod and plug were threaded so that the point of contact could be varied readily. The lower half of the regulator was sealed and kept at constant pressure during a run by immersing it in a thermostat which was maintained at any convenient temperature, usually about 25° C. in the winter months and 30° C. in the summer. The upper half was connected to the system containing the boiling tube. When the pressure in this part of the system fell below 760 mm. the diaphragm was forced up so that it closed the circuit operating the relay R which, in turn, closed the circuit to the electromagnet F causing the valve E to be opened, admitting a puff of air from the high pressure reservoir. As soon as the pressure had been raised to 760 mm. the contact at the diaphragm was broken, causing

the magnet circuit to be broken so that the spring could close the valve E. This regulation was best if a small leak was provided in the bottle H so that the valve was operated every few seconds. When there were no disturbing factors in this system, the pressure could be maintained constant to one or two hundredths of a millimeter of mercury. Sometimes the regulation,as shown by the manometer M, when a liquid was boiling in L was not as good as this but this was due to irregularities in the rate of boiling and the variations in pressure dod not last long enough to affect the boiling point of the liquid more than one-thousandth of a degree.

The apparatus used to determine the vapor compositions was essentially the same as that described by Rosanoff.[54] with a few slight modifications. The boiling tube was surrounded by a vapor thermostat, which could be adjusted to any temperature either by changing the composition of the liquid or by varying the pressure. All the distillations were run at 760 mm. pressure, using the regulator described by Mathews and Faville.[55] The analysis of the distillates from the chloroform-acetone mixtures was done with a Pulfrich refractometer and for those from the alcohol-water mixtures with the Zeiss immersion refractometer, using the auxiliary prism. The analysis thus performed required only a small quantity of liquid. The temperature was controlled for measure-

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54. Loc. cit.
55. J. phys. chem. 21 1 (1917)

ments with the Pulfrich by pumping water from a thermostat, maintained at 25° C., through the water-jacket on the instrument. For the measurements with the Zeiss refractometer, the end of the instrument was simply dipped into a thermostat at 30° C.

Procedure in Determining a Molecular Elevation.

The liquid was weighed in a weight pipette and then introduced into the boiling tube. The current was adjusted so as to give a steady rate of boiling and the mixture allowed to boil until equilibrium was reached between the liquid and vapor which usually required from half an hour to an hour. If there was any superheating, this could generally be eliminated by sending a heavy current through the heating coil. As soon as equilibrium was reached, the thermometer was read every minute for half an hour. At ten-minute intervals, the current was increased three or four amperes for a few seconds. This caused a small temporary change in the thermometer reading, thus preventing an error from being introduced due to the mercury hanging in the stem of the thermometer. Having obtained the boiling point of the mixture, the heating circuit was broken and a weighed quantity of solute introduced into the tube be removing the thermometer. The boiling point of this solution was then determined in the same manner as that of the original liquid. A second portion of solute was in-

troduced and the boiling point determined. If this did not give a rise of seventy-five hundredths of a degree or more or if the three points did not give a good straight line, a third portion of solute was added. Finally, before the boiling was stopped, two samples of the solution were drawn off and analyzed so as to obtain the effective concentration. This corrected for the vapor in the vessel and condensed liquid on the walls of the vessel and condenser.

A typical determination for a chloroform-acetone mixture follows:

(Note: In weighing the liquids a glass counterpoise was used so that the weights recorded are the differences in weight between the counterpoise and the pipette containing the liquid)

Weight of pipette and chloroform	55.33	gms.
Weight of pipette and residue	5.80	gms.
Weight of chloroform used	49.53	gms.

Weight of pipette and acetone	52.98	gms.
Weight of pipette and residue	18.90	gms.
Weight of acetone used	34.08	gms.

Composition of liquid 59.2% $CHCl_3$ 40.8% Me_2CO

Bottle number	619	72	61
Weight of bottle and camphor	7.8494	8.3474	7.3406
Weight of bottle	6.1902	7.2486	6.1182
Weight of camphor	1.6592	1.0988	1.2224

Boiling point of mixture 62.38° C.

Room temperature 25° C.

Heating current in apparatus 9 amps.

Time	0 gms.	Time		Time	1.2224 gms.
2:30	2.687	Raised	Current	3:35	2.896
1	2.687	2:50	2.690		2.896
2	2.687		2.690		2.896
3	2.687		2.690		2.896
4	2.687		2.690		2.896
2:35	2.687		2.690	3:40	2.896
6	2.687	2:55	2.690		2.896
7	2.687		2.690		2.896
8	2.687		2.690		2.896
9	2.687	Raised	Current	Raised	Current
Raised	Current		2.690		2.897
2:40	2.690		2.690	3:45	2.897
	2.690	3:00	2.690		2.897
	2.690		2.690		2.897
	2.690		2.690		2.897
	2.690				2.897
2:45	2.690			3:50	2.897
	2.690				2.897
	2.690				2.897
	2.690				
	2.690				

Raised Current	
	2.901
	2.900
3:55	2.900
	2.900
	2.900
	2.900
	2.900
4:00	2.900
	2.900
Raised Current	
	2.900
	2.900
	2.900
4:05	2.900
	2.900
	2.900
	2.900

Time	2.8816 gms.
4:45	3.208
	3.210
	3.210
	3.210
	3.210
4:50	3.210
	3.210
	3.210
Raised Current	
	3.197
	3.197
4:55	3.197
	3.192
	3.192
	3.192
	3.192
5:00	3.192
	3.192
	3.192
	3.192
Raised Current	
	3.191
5:05	3.191
	3.191
	3.191
	3.191
	3.191
5:10	3.191
	3.191
Raised Current	
	3.192
	3.191
	3.191
5:15	3.191
	3.191
	3.191

Time	3.9804 gms.				
5:55	3.388		3.390		3.390
	3.388		3.390	6:10	3.390
	3.388		3.390		3.390
	3.388	6:05	3.390		3.390
	3.388		3.390		3.390
6:00	3.390	Raised Current			3.390
	3.390		3.391	6:15	3.390
			3.390		3.390

Samples for analysis	619	61
Weight of bottle and solution	11.1055	11.1895
Weight of bottle	6.1902	6.1182
Weight of solution	4.9153	5.0713

Sample number		61	619
Polarimeter readings (average)	right	334.293	334.216
	left	154.413	154.334
Zero reading	right	332.690	332.690
	left	152.810	152.810
Rotation		1.603	1.525
Grams of camphor		.2561	.2436
Grams of camphor per 100 grams solvent		5.32	5.21
Average		5.26	

The results obtained for the elevation of the boiling point for different mixtures of chloroform and acetone are summarized in the following table:

% CHCl$_3$	% Me$_2$CO	b.p.	Gm. camphor added	Corrected temperature	Δt	Wt. of sample	Gms. Camphor	Conc.		K
100	0	61.09	0	3.111		4.484	.2190	5.12)	4.98	36.1
			3.0056	3.764	.653	4.682	.2158	4.85)		37.2
			5.6212	4.329	1.218					
79.7	20.3	64.22	0	2.379		5.885	.2978	5.34)	5.43	30.85
			1.5498	2.774	.395	5.878	.3098	5.53)		
			2.9575	3.082	.703					
			4.7390	3.483	1.104					
74.7	25.3		0	2.552		5.798	.245	4.42)	4.61	27.15
			2.0142	2.971	.419	5.863	.268	4.80)		
			3.8426	3.376	.824					
68.9	31.1	63.44	0	3.743		5.312	.2083	4.07)	4.13	22.0
			1.0019	3.895	.152	5.221	.2103	4.19)		
			2.4082	4.121	.378					
			3.6176	4.341	.598					

% $CHCl_3$	% Me_2CO	b.p.	Gm. camphor added	Corrected temperature	Δ t	Wt. of sample	Gms. Camphor	Conc.		K
59.2	40.8	62.38	0	2.695		4.915	.2436	5.21)	) 5.26	20.22
			1.2224	2.905	.210	5.071	.2561	5.32)		
			2.8816	3.197	.502					
			3.9804	3.393	.698					
50	50	61.31	0	2.581		5.486	.2838	5.45)	) 5.48	20.15
			1.5157	2.838	.257	4.636	.2420	5.51)		
			2.7564	3.027	.446					
			4.3789	3.306	.725					
40.2	59.8	60.11	0	3.508		4.440	.2648	6.33)	) 6.35	17.83
			1.7088	3.760	.252	5.400	.3228	6.38)		
			3.1621	4.023	.515					
			5.2573	4.251	.743					
30.1	69.9	58.93	0	2.343		4.628	.3109	7.20)	) 7.22	17.15
			2.1008	2.645	.302	4.936	.3335	7.23)		
			4.1480	2.917	.574					
			5.9432	3.158	.815					

% $CHCl_3$	% Me_2CO	b.p.	Gm.camphor added	Corrected temperature	Δ t	Wt. of sample	Gms. Camphor	Conc.		K
19.9	80.1	57.76	0	3.026		4.251	.2710	6.82)	6.85	16.40
			1.9735	3.440	.414	3.631	.2332	6.87)		
			3.4765	3.765	.739					
10.3	89.7	57.02	0	2.452		3.716	.2963	8.66)	8.64	14.92
			2.6247	2.918	.466	3.768	.2991	8.62)		
			4.7035	3.299	.847					
0	100	56.12	0	3.155		4.116	.450	12.25)	12.37	14.80
			1.9762	3.550	.395	4.197	.467	12.50)		
			4.0609	3.966	.811					
			6.0596	4.364	1.209					

The concentrations are given in grams of camphor in one hundred grams of solvent. The last column is therefore the elevation produced by the addition of one gram molecule of solute to one hundred grams of solvent. A second run on the 40 per cent chloroform 60 per cent acetone mixture gave a value of 17.82 which agrees very well with that obtained on the first run. In the case of the 100 per cent chloroform, the circumstances attending the analysis of the samples of the solution were such that the higher concentration giving a value of 36.1 for K is believed to be the best analysis.

The elevations for the alcohol-water mixture were obtained in a manner similar to that used for the chloroform-acetone mixtures. One marked difference between the two pairs in making these determinations was that the alcohol-water mixtures reached equilibrium with the vapor much more rapidly than did the chloroform-acetone, thus enabling most of the runs to be completed in four or five hours instead of six or seven as often happened with the chloroform-acetone. A typical run for an alcohol-water mixture follows:

Weight of pipette and water	14.49	grams
Weight of pipette and residue	6.00	"
Weight of water used	8.49	"

Weight of pipette and alcohol	56.58 grams
Weight of pipette and residue	5.98 "
Weight of alcohol used	49.60 "

Composition of the liquid 85.4% alcohol 14.6% water.

Bottle number	65	66
Weight of bottle and acetamide	8.1454	8.5524
Weight of bottle and residue	6.5387	6.7345
Weight of acetamide added	1.6067	1.8179

Boiling point of the mixture 78.4° C.

Room temperature 28° C.

Heating current 10 amps.

Temperature readings

Time	0 gms.				
2:45	3.551	4	3.551		3.550
6	3.551	Raised Current			3.550
7	3.551	2:55	3.551		3.550
8	3.551		3.550	3:05	3.550
9	3.551		3.550		3.550
2:50	3.551		3.550		3.550
1	3.551		3.550		3.550
2	3.551	3:00	3.550		3.550
3	3.551		3.550		

Time	1.6067 gms.	Time	3.4246 gms.		
3:25	3.964	4:05	4.450	4:25	4.455
	3.964		4.450		4.455
	3.964		4.450		4.455
	3.964		4.450		4.455
	3.964		4.450		4.455
3:30	3.964	4:10	4.450	4:30	4.455
	3.964		4.450		4.455
	3.964		4.450		4.455
	3.964		4.450		4.455
	3.964		4.450		4.455
Raised Current		Raised Current			
3:35	3.964	4:15	4.454		
	3.964		4.454		
	3.964		4.454		
	3.964		4.454		
	3.964		4.454		
3:40	3.964	4:20	4.454		
	3.964		4.454		
	3.964		4.454		
	3.964		4.454		
	3.964		4.454		
3:45	3.964				
	3.964	Raised Current			
	3.964				
	3.964				
	3.964				

Samples for analysis	650	669
Weight of bottle and solution	10,575	10,551
Weight of bottle	6,504	6,696
Weight of solution	4,071	3,855
Alkali used in titration of excess acid	17.00 cc.	18.65 cc.
Alkali used for blank	42.00 "	42.00 "
Alkali equivalent to acid neutralized by the ammonia distilled off	25.00 "	23.35 "
Gms. acetamide represented	.2370	.2215
Gms. acetamide in 100 gms. solvent	6.19	6.11
Average	6.15	

Summary of the Determination:

Grams of acetamide added	0	1.6067	3.4346
Corrected boiling point	3.548	3.967	4.463
Temperature rise		.419	.915
Final concentration of acetamide in gms. per 100 gms solvent			6.15
Molecular elevation for the mixture			8.79

The results obtained for the elevation of the boiling point for different mixtures of alcohol and water are summarized in the following table.

% EtOH	% H_2O	b.p.	Gms. acetamide	Corrected temperature	Δ t	Wt. of sample	Gms. acet.	Conc.		K
100	0	78.3	0	2.439		3.629	.2154	6.30)	6.27	10.71
			1.3997	3.021	.582	3.368	.1970	6.22)		
			2.7461	3.580	1.141					
95.4	4.6	78.2	0	3.602		3.618	.2080	6.10)	6.17	10.22
			1.6797	4.114	.512	3.754	.2200	6.24)		
			3.2455	4.669	1.067					
90.4	9.6	78.3	0	3.446		3.356	.1530	4.78)	4.78	9.60
			.7549	3.702	.256	3.493	.1591	4.78)		
			1.4855	3.964	.518					
			2.2399	4.224	.778					
85.4	14.6	78.4	0	3.548		4.071	.2370	6.19)	6.15	8.79
			1.6067	3.967	.419	3.855	.2215	6.11)		
			3.4246	4.463	.915					
80.1	19.9	78.7	0	4.074		3.667	.1683	4.81)	4.76	8.03
			1.0034	4.343	.269	3.700	.1664	4.71)		
			2.3592	4.723	.649					

% EtOH	% H_2O	b.p.	Gms. acetamide	Corrected temperature	Δ t	Wt. of sample	Gms. acet.	Conc.		K
74.8	25.2	78.8	0	3.838		3.907	.2712	6.94)	) 6.93	7.80
			1.2507	4.109	.271	4.067	.2816	6.92)		
			2.5155	4.408	.570					
			4.0420	4.755	.917					
57.8	42.2	80.6	0	4.299		3.651	.1630	4.68)	) 4.73	7.48
			1.0648	4.560	.261	3.640	.1664	4.79)		
			2.4327	4.899	.600					
50.2	49.2	81.5	0	3.264		3.949	.2068	5.24)	) 5.18	7.57
			1.3424	3.502	.238	3.693	.1896	5.13)		
			2.3762	3.712	.448					
			3.4636	3.926	.662					
36.5	63.4	83.1	0	4.229		3.849	.1889	5.16		
			1.3350	4.553	.324	3.447	.1554	4.70		7.80
			2.5584	4.851	.622					

% EtOH	% H_2O	b.p.	Gms. acetamide	Corrected temperature	Δ t	Wt. of sample	Gms. acet.	Conc.		K
35.5	64.5	83.2	0	3.224		4.066	.2405	6.31		
			1.9248	3.663	.439	3.909	.2395	6.52		7.98
			3.8820	4.105	.881					
30.2	69.8	84.2	0	2.406		4.123	.2350	6.07		8.79
			2.1148	2.882	.476	4.327	.2478	6.08		
			4.0310	3.309	.903					
24.3	75.7	85.5	0	3.115		4.327	.2444	5.99)	) 5.92	10.40
			1.2400	3.517	.402	4.735	.2621	5.86)		
			2.5904	3.893	.778					
			3.5528	4.160	1.045					
13.7	86.3	89.5	0	3.135		4.256	.1914	4.49)	) 4.54	11.48
			1.4276	3.602	.467	4.616	.2123	4.58)		
			2.7627	4.016	.881					

% EtOH	% H_2O	b.p.	Gms. acetamide	Corrected temperature	Δ t	Wt. of sample	Gms. acet.	Conc.		K
9.31	90.69	92.4	0	2.678		4.248	.2740	6.88)	6.84	10.32
			2.3530	3.310	.632	4.358	.2775	6.81)		
			4.5718	3.876	1.198					
6.44	93.56	94.5	0	3.761		4.774	.2215	4.87)	4.90	10.35
			1.6691	4.203	.442	4.628	.2175	4.93)		
			3.3187	4.620	.859					
2.1	97.9	97.1	0	3.067		4.710	.1867	4.13)	4.10	8.71
			1.3202	3.374	.307	4.633	.1820	4.08)		
			2.5336	3.675	.608					
0	100	100	0	4.257		4.500	.2859	6.79)	6.86	5.15
			1.3414	4.433	.176	5.066	.3288	6.94)		
			2.9471	4.666	.409					
			4.4525	4.858	.601					

In two cases which are marked (1) in the table, difficulties arose during the analysis so that although the results are recorded, the probable error os so great that only the result obtained from the other sample has been considered. For some unknown reason the analysis of the samples for the mixture containing 6.44 per cent alcohol gives too low a result; the concentration of the solution as made up was 5.1 grams of acetamide in 100 grams of solvent, which gives a value of 9.93 for K. Using this value, the point in question is in accord with the others on the curve. The results which have just been given for the pairs chloroform-acetone and alcohol-water are shown graphically in the curves, Plates I and II.

Vapor Compositions.

The composition of the vapor is equilibrium with a given mixture and also of the vapor in equilibrium with five and ten per cent solutions of acetamide in that mixture was determined. For this purpose a quantity of the mixture, sufficient for the three runs, was made up in a weight pipette from which the liquid necessary for the first run was weighed into the apparatus. The vapor thermostat was then adjusted to the desired temperature and the distillation started. The distillate was collected in four weighing bottles and analyzed by refractive index measurements. The compositions of the four distillates were plotted against

the average per cent distilled and the curve extended to zero distillate, thus giving the composition of the vapor that first comes off.

Acetamide or camphor, as the case might be, was then added to the liquid remaining in the pipette so as to make a five per cent solution and the composition of the vapor coming off from this determined as before. The third portion of liquid was finally brought to a concentration of 10 per cent acetamide or camphor and the vapor composition again determined. The results are shown graphically in Plates III - VI. The date necessary for a determination is shown by the following run with one of the alcohol-water mixtures:

Composition of the mixture 18.9% alcohol 81.1% water

Weight of liquid used 23.04 gms.

Distillates	Wt.	Mean % distilled	Zeiss reading	% EtOH
First	1.9320	4.16	88.19	65.6
Second	2.1272	13.0	87.16	61.25
Third	1.7558	21.5	83.45	53.0
Fourth	1.6466	28.8	69.38	36.0

% EtOH at zero distillate 67.0 %.

With the chloroform-acetone mixtures, the readings for the refractive index were expressed in degrees as read

from the Pulfrich. The date for the chloroform-acetone mixtures is summarized in the following table:*

% $CHCl_3$	% Me_2CO	% $CHCl_3$	% Me_2CO	% $CHCl_3$	% Me_2CO	% $CHCl_3$	% Me_2CO
91.08	8.92	93.3	6.7	92.7	7.3	91.9	8.1
82.20	17.80	83.0	17.0	81.5	18.5	80.3	19.7
71.95	28.05	68.8	31.2	67.3	32.7	66.2	33.8
62.7	37.3	55.9	44.1				
61.2	38.8			53.6	46.4	51.3	48.7
50.4	49.6	41.5	58.5	39.9	60.1	39.0	61.0
40.1	59.9	29.5	70.5	29.0	71.0	28.6	71.4
38.8	61.2	27.9	72.1				
26.6	73.4	16.3	83.7	15.1	84.9	14.9	85.1
8.8	91.2	6.3	93.7	5.8	94.2	5.1	94.9

The effect of the addition of camphor may be shown a little better by comparing the excess of acetone in the vapor in the three cases. The following table gives these excesses:

% Me_2CO in Liquid	Excess in vapor		
	0 camphor	5%	10%
8.92	- 2.22	- 1.62	- 0.82
17.80	- 0.80	+ 0.70	+ 1.9
28.05	+ 3.15	4.65	5.75
37.3	6.8		
38.8		7.6	9.9
49.6	8.9	10.5	11.4
59.9	10.6	11.1	11.5

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* Data obtained by B. H. Carroll.

Table continued.

% Me_2CO in liquid	Excess in vapor		
	0 camphor	5%	10%
61.2	10.9		
73.4	10.3	11.5	11.7
91.2	2.5	3.0	3.7

For the alcohol-water mixtures we have the following:

Liquid		Vapor					
		0 solute		5% solute		10% solute	
%EtOH	%H_2O	%EtOH	%H_2O	%EtOH	%H_2O	%EtOH	%H_2O
10.7	89.3	55.0	45.0	50.8	49.2	46.2	53.8
18.9	81.1	67.0	33.0	64.5	35.5		
20.3	79.7					63.9	36.1
29.6	70.4			73.6	26.4	73.3	26.7
31.2	68.8	73.8	26.2				
38.4	61.6	77.8	22.2	77.8	22.2	77.8	22.2
50	50	78.2	21.8	78.0	22.0	78.3	22.0
60	40	78.6	21.4				
67.2	32.8	81.0	19.0				
79.5	20.5	84.7	15.3				
90.7	9.3	91.0	9.0				

In mixtures containing more than fifty per cent alcohol, the composition of the vapor in equilibrium with the solutions did not differ appreciably from that in equilibrium

with the mixtures containing no solute. The excess of alcohol in the vapor is given in the following table:

% EtOh in liquid	Excess in vapor 0 solute	5%	10%
10.7	44.3	40.1	35.5
18.9	48.1		
20.3			43.6
29.6		44.0	43.7
31.2	42.6		
38.4	39.4	39.4	39.4
50.	28.2	28.0	28.3
60.	18.6		
67.2	13.8		
79.5	5.2		
90.7	.3		

In making the analyses for the vapor compositions, it was necessary to make up refractive index curves for the mixtures. The chloroform-acetone curve is given for the helium line 587 u u at 25° C.

% $CHCl_3$	% Me_2CO	N
100	0	1.44284
91.1	8.9	1.43026
82.2	17.8	1.41832
71.95	28.05	1.40684
61.2	38.8	1.39631
50.4	49.6	1.38714
38.8	61.2	1.37818
26.6	73.4	1.37069
13.1	86.9	1.36324
0	100.	1.35606

For the alcohol-water mixtures, the values given are the reading on the Zeiss immersion refractometer at 30° C.

% EtOH	% H_2O	Zeiss reading
0	100.	11.89
10.7	89.3	29.68
18.9	81.1	45.10
31.2	68.8	63.41
39.0	61.0	72.70
49.3	50.7	80.91
60.0	40.0	86.70
67.2	32.8	88.89
79.5	20.5	90.30
83.8	16.2	89.70
88.7	11.3	88.00
95.95	4.05	83.92
97.52	2.48	82.71
100.	0	80.20

As there was a marked difference in the rate at which the acetamide went into solution in the alcohol and water at room temperature, it was decided to investigate its solubility. The solubility of acetamide in alcohol is given by Speyers.[56]

Temp.	Mol. % Acetamide	Gms. Acetamide in 100 gms. EtOH
62.0	78.92	478
42.5	56.06	164
18.6	32.87	62.5
0.0	18.58	29.0

Determinations were made of the solubility of acetamide in water at 24.5° C. and 0.3° C. At 24.5° C., 238 grams of acetamide dissolved in 100 grams of water and at 0.3° C., 152 grams of acetamide dissolved. These figures show that at the lower temperatures acetamide is much more soluble in water than in alcohol but as the temperature is raised, the solubility in alcohol increases much more rapidly than the solubility in water. From the standpoint of the reaction isochore, this means that the heat of solution of acetamide in alcohol is greater than the heat of solution in water.

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[56] Sill Journ. (4) 14 295 (1902)

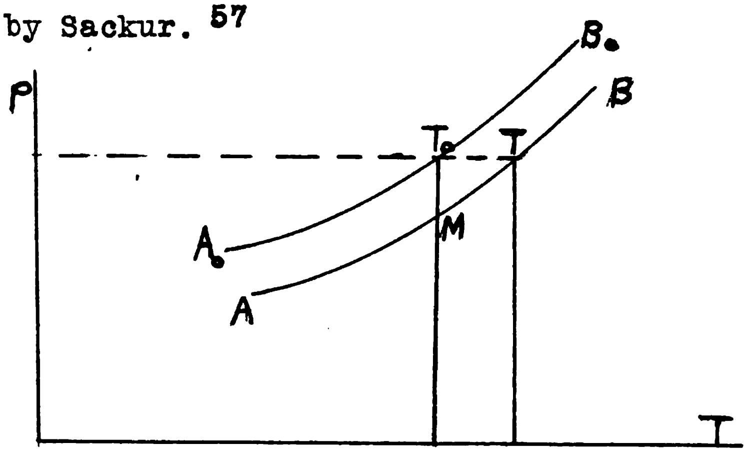
Discussion of Results

The first thing that stands out in the results is that the values obtained for the molecular elevations of the pure liquids are lower than those reported by other investigators. This can be accounted for at least partially as due to the fact that in the present work, the concentration producing the observed elevation of the boiling point was determined by analyzing a sample drawn from the boiling solution, thus obtaining the true concentration in the boiling liquid instead of calculating the concentration from the weights of liquid and solute used. This correction has either been entirely neglected in previous work or has been subject to a purely arbitrary correction. In addition to this fact, the pressure regulation and method of heating used in the present work enabled the temperatures to be determined much more exactly by eliminating variations in barometer pressure and by eliminating superheating.

These reasons, however, cannot be advanced to explain the differences between the observed values of K and those calculated by means of the vant Hoff equation $K = \frac{RT^2}{L}$ where T is the absolute temperature of ebullition, R the gas constant and L the heat of vaporization of the liquid. The values are compared in the following table.

Liquid	K obs.	K calc. $\frac{RT^2}{L}$
Chloroform	36.1	37.8
Acetone	14.80	17.13
Ethyl alcohol	10.71	11.85
Water	5.15	5.13

It is to be noted that in every case, except water, the observed value of K is lower than that calculated by vant Hoff's equation. This would seem to indicate that either some unjustifiable assumption was used in the derivation of the equation or a systematic error occurred in the experimental work. Let us first investigate the derivation of the equation as given by Sackur.[57]



Let A_0 B_0 be the vapor pressure curve of the pure solvent and A B that of the solution and T_0 and T be the boiling points of the pure solvent and solution respectively. Then if we consider a case where $T - T_0$ and $p - p_0$ are so small that

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[57] Thermochemistry and Thermodynamics p. 230 and 254

the portion of the curve M T may be taken as a straight line, we have:

$$\frac{T\ T_o}{T_o\ M} = \cot M\ T\ T_o = \frac{1}{\tan M\ T\ T_o}$$

or

$$\frac{T - T_o}{p_o - p} = \frac{1}{\tan M\ T\ T_o}$$

Now $\tan M\ T\ T_o$ is the slope of the vapor pressure curve and according to the differential calculus, this is given by $\frac{d\ p}{d\ T}$.

Substituting:

$$\frac{T - T_o}{p_o - p} = \frac{1}{\frac{d\ p}{d\ T}} \qquad (1)$$

The Clausius-Clapeyron equation states that

$$\frac{d \ln p_o}{d\ T} = - \frac{L}{R\ T^2}$$

or

$$\frac{1}{p_o}\ \frac{d\ p}{d\ T} = - \frac{L}{R\ T^2}$$

whence

$$\frac{d\ p}{d\ T} = - \frac{L\ p_o}{R\ T^2}$$

Inserting this value in (1) and solving for $T - T_o$ we have

$$T - T_o = - \frac{R\ T^2}{L} \cdot \frac{p_o - p}{p_o} \qquad (2)$$

Now for dilute solutions it may readily be shown, by an application of Raoult's law, that

$$\frac{p_o - p}{p} = \frac{c}{c_o}$$

where c_o is the number of mols in unit volume of solution and c is the number of mols of solute in unit volume of solution. Introducing this into (2) we obtain

$$T - T_o = - \frac{R T^2}{L} \frac{c}{c_o} = - \frac{R T^2 c}{L'}$$

where L' is the heat of evaporation of unit volume of solution. The molecular elevation of the boiling point is given by

$$K = \frac{T - T_o}{c} = - \frac{R T^2}{L}$$

The question now arises as to what approximations have been used and to what extent do they affect the final result. The first approximation made was that the vapor pressure curve is a straight line over the temperature range considered. That this is not strictly true is apparent from an inspection of the vapor pressure curves of liquids at their boiling points but this error may be reduced considerably by taking smaller values of $T - T_o$. It seems therefore that there must be some other approximation which is more responsible for the deviation. In passing from equation (1) to (2) the Clausius equation has been introduced in the form

$$\frac{d p}{d T} = - \frac{L p_o}{R T^2}$$

Now to obtain this equation, it is assumed that the vapor behaves as an ideal gas. Experimentation, however, has shown that no gas is an ideal gas and that vapors in the neighborhood

of their condensing points are apt to deviate considerably from the ideal gas laws. This would seem to be a rather serious approximation to introduce into an equation which is to be used to check accurate experimental date. On the theory that this is where the approximation comes in, let us return to equation (1) and see what results this will give when applied to the calculation of $T - T_0$.

The values of $\frac{dp}{dT}$ may be obtained graphically by plotting the vapor pressure curve from date obtainable in Landolt-Börnstein's "Tabellen" and finding the slope of the tangent to the curve at the boiling point. For $p_0 - p$, we may apply Raoult's law thus

$$\frac{p_0 - p}{p_0} = \frac{n}{N + n}$$

whence $$p_0 - p = \frac{n p_0}{N + n}$$

The value of $T - T_0$ is given by $$T - T_0 = \frac{p_0 - p}{\frac{dp}{dT}} \qquad (3)$$

Applying this to the alcohol, we find from the vapor pressure data available that $\frac{dp}{dT}$ is 29.9 mm. per degree. The values for n and N as used were .106 and 2.175 respectively and these gave po - p as 35.34 mm. Substituting in (3), we obtain 1.182 for $T - T_0$ as compared to the observed value 1.141. The molecular elevation corresponding to the calculated value of $T - T_0$ is 11.12 which agrees better with the experimental

data than the value calculated by $\frac{R\,T^2}{L}$. The same calculation was carried out with acetone, chloroform, and water with the results shown in the following table:

Liquid	K from $\frac{R\,T^2}{L}$	K from $\frac{po-p}{dp/dT} \cdot \frac{M}{G}$	K obs.
Chloroform	37.8	33.4	36.1
Acetone	17.13	18.0	14.80
Ethyl alcohol	11.85	11.12	10.71
Water	5.13	4.97	5.15

Except in the case of acetone, the values calculated by the second method are appreciably lower than those calculated by the vant Hoff equation. When values in the second column are compared with the observed values of K, we see that in two cases the observed value is too high and in two cases too low, The experimental data necessary for the calculation is best known in the case of water and quite well known in the case of alcohol, but for chloroform and acetone, the vapor pressure data is rather scanty, the values available being at ten degree intervals. There are therefore chances of a considerable error coming in in the determination of the slope of the curve at the boiling point. To be sure, some of the discrepancy between observed and calculated values can be accounted for on the grounds that the vapor pressure curves are not straight lines over the temperature ranges considered, but that deviation is nowhere near enough to account for the disagreement in the case of the chloroform and acetone. A more

accurate calculation of the value of K will have to be left until either $\frac{dp}{dT}$ is determined more accurately than it is known at present or until the deviations of the vapors from the gas laws are known. The experimental evidence, however, is such that we may say $K = \frac{f(T)}{L}$ where f (T) is probably a quadratic.

Let us now pass to a consideration of the elevations produced in the boiling points of the mixtures. In such a case, the value of K will depend on three factors: (1) the values of K for the components of the mixture, (2) the heat of mixing, (3) the relative affinity of the components for the solute added. The first of these is evident, the second comes in from a consideration of $K = \frac{f(T)}{L}$. For a mixture, the value of L required by this equation will be the sum of the heats of vaporization of the components and the heat of mixture, i.e., we may write the heat of vaporization of the mixture as $c_1 L_1 + c_2 L_2 + L_m$ where c_1 and c_2 are the amounts of the components 1 and 2 in unit volume of mixture and L_m is the heat absorbed on mixing these two liquids at the boiling point of the mixture. Then if heat is evolved on mixing the total heat of vaporization is higher than calculated from the simple rule of mixtures and therefore K should be lower than calculated in the same way. It also follows that if heat is absorbed on mixing, the heat of vaporization of the mixture will be lower than given by the rule of mixtures and therefore

K will be higher. If heat of mixture is an indication of compound formation and reaches a maximum at the composition of a compound, then the value of K should show a maximum deviation from the mixture rule at that same composition. In the case of chloroform and acetone mixtures, we find a maximum deviation from a straight line at about 66 per cent chloroform corresponding to $CHCl_3 - CH_3COCH_3$ which is the compound which has actually been isolated from this mixture. The deviation is in the right direction also since there is considerable heat evolved on mixing equal molar quantities of the two liquids. For the alcohol-water curve, the maximum deviation on one side of the straight line comes at 79 per cent alcohol by weight corresponding to the maximum index of refraction and maximum volume change as reported by Holmes.[58] The deviation, however, does not agree with the heat of mixture as reported by Bose[59] since he says that at 74° C., the heat of mixing of such a mixture is negative and therefore the value of K should be greater than that given by the straight line relation instead of less. The calculations of Masing, on the other hand, give a value for the heat of vaporization of a fifty-fifty mixture as higher than calculated by the rule of mixtures. This would mean a lower value of K which agrees with the experimental facts. There remains the possibility, however, that there is a compound formed which causes a change in f (T) so as to overbalance the effect due to the heat of mixing. On the other end

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[58] Loc. cit.
[59] Loc. cit.

of the alcohol-water curve, there is a very pronounced deviation in the other direction but this can be discussed better in connection with the third factor.

The third factor affecting the elevation of the boiling point as already stated is the relative affinity of the solvents for the solute. To see what this does, let us imagine a few solute molecules dispersed in a large number of molecules of the components of the mixture. If neither type of solvent molecules has any specific attraction for the solute, then the vapor pressure will be lowered in such a way that the composition of the vapor in equilibrium with the solution will be the same as that in equilibrium with the mixture before the solute is added. If this is not true, but one of the solvents has a greater affinity for the solute than the other, then the partial vapor pressure of this component will be lowered more than it would be if no such affinity existed. The composition of the vapor, therefore, would be changed by the addition of a solute. The result would be that the observed elevation of the boiling point would be either abnormally high or abnormally low, depending on which component was affected the most. Let us see how this theory stands in the light of experimental evidence. In the case of the alcohol-water mixtures, it was found that in mixtures containing small quantities of alcohol, the addition of acetamide lowered the partial pressure of the alcohol in the vapor considerably and in the same region, the observed value of

K rose sharply to a maximum, indicating that the alcohol has a greater affinity for acetamide than the water. We may secure evidence of this greater affinity from the solubility measurements which have been given. If we apply the integrated form of the reaction isochore to those measurements, we find that acetamide has a higher heat of solution in alcohol than in water, so that if we apply Berthelot's principle (this applies only at absolute zero but may be taken as giving a rough indication of the facts at higher temperatures) the alcohol has a greater affinity for the acetamide than the water. These facts which have just been given amount to saying that we have such a thing as a partition coefficient in completely miscible liquids. This being true, the curve obtained connecting K with the composition of the mixture will vary in shape, depending on what solute is used, the effect due to the nature of the solute disappearing only when the vapor composition is the same for the mixture before and after adding solute.

Let us attempt the calculation of the distribution of acetamide between alcohol and water in a mixture containing 20 per cent alcohol. By means of the vapor composition curve, it is readily calculated that the partial pressure of the alcohol over this mixture is 345 mm. and that of the water 415 mm. Over the ten per cent solution of acetamide in this mixture, the partial pressures were found to be 307 and 453

for the alcohol and water respectively. The temperature in the second case was higher, so these pressures must be reduced to the same temperature that the first measurements were made at. If we assume that the rule of mixtures holds for $\frac{d\,p}{d\,T}$, then for a mixture containing 20 per cent alcohol, $\frac{d\,p}{d\,T}$ is 28.0, since the values for water and alcohol are 27 and 32 respectively. The lowering due to the addition of ten per cent acetamide to the mixture can be calculated from this, by using the value of K as read from the graph. The equation is

$$p_o - p = \frac{10}{59}\ K\ \frac{d\,p}{d\,T}$$

which gives $p_o - p$ as 52.5 mm. The total pressure of the vapor over the solution at the boiling point of the solvent is therefore 707.5 . Now, for the small change in temperature involved, we may consider the vapor composition as unchanged without making any great error, so this 707.5 mm. is split up in the ratio of 307 to 453. This gives 286 mm. for the partial pressure of the alcohol in the vapor and 421.5 mm. for the water. We see then that the partial pressure of the alcohol has been lowered 59 mm., whereas the partial pressure of the water has increased 6 mm. This increase in the partial pressure of the water vapor may be explained by considering that we have alcohol dissolved in the water lowering its vapor pressure; then the acetamide is introduced and takes some of

the alcohol away from the water, thus tending to cause the vapor pressure of the water to rise. In this particular case, the effect is so great that it overbalances the lowering which the acetamide dissolved in the water would produce. Now, if we apply Raoult's law to the partial pressure of the alcohol, we obtain

$$\frac{59}{345} = \frac{n}{N + n} \qquad \text{whence} \qquad 59N = 286\ n$$

so that there are 4.85 mols of alcohol to one mol of acetamide or .21 mols acetamide in one of alcohol. For a 10 per cent solution of acetamide in a mixture containing 20 per cent alcohol, this amounts to 54 per cent of the acetamide in the alcohol, which at least is something within reason and seems to support the view that such a distribution actually takes place.

In the case of the chloroform-acetone mixtures, there is also a change in the vapor composition on adding the solute but the change is much smaller than for the alcohol and water mixtures, so the effect is not so pronounced. According to the data obtained, the partial pressure of the chloroform is lowered the most, which would tend to shift the elevation curve upward. As the effect of the solute on the vapor composition is fairly uniform for all the mixtures, this displacement of the curve is general and does not produce any marked deformation in the curve.

Summary and Conclusions

The molecular elevations of the boiling point have been determined for chloroform, acetone, ethyl alcohol and water and the observed values compared with those calculated by means of the equations $K = \frac{R T^2}{L}$ and $K = \frac{p_o - p}{\frac{dp}{dT}} \cdot \frac{M}{G}$ and the deviations have been discussed.

The elevations produced in the boiling points of mixtures of chloroform and acetone, on adding camphor and of mixtures of alcohol and water on adding acetamide have been determined and the factors affecting these elevations have been discussed.

It has been shown that there are grounds for believing that such a thing as a partition coefficient exists for a solute in a mixture of two completely miscible liquids.

The vapor composition and refractive index curves have been determined for the pairs chloroform-acetone and alcohol-water.

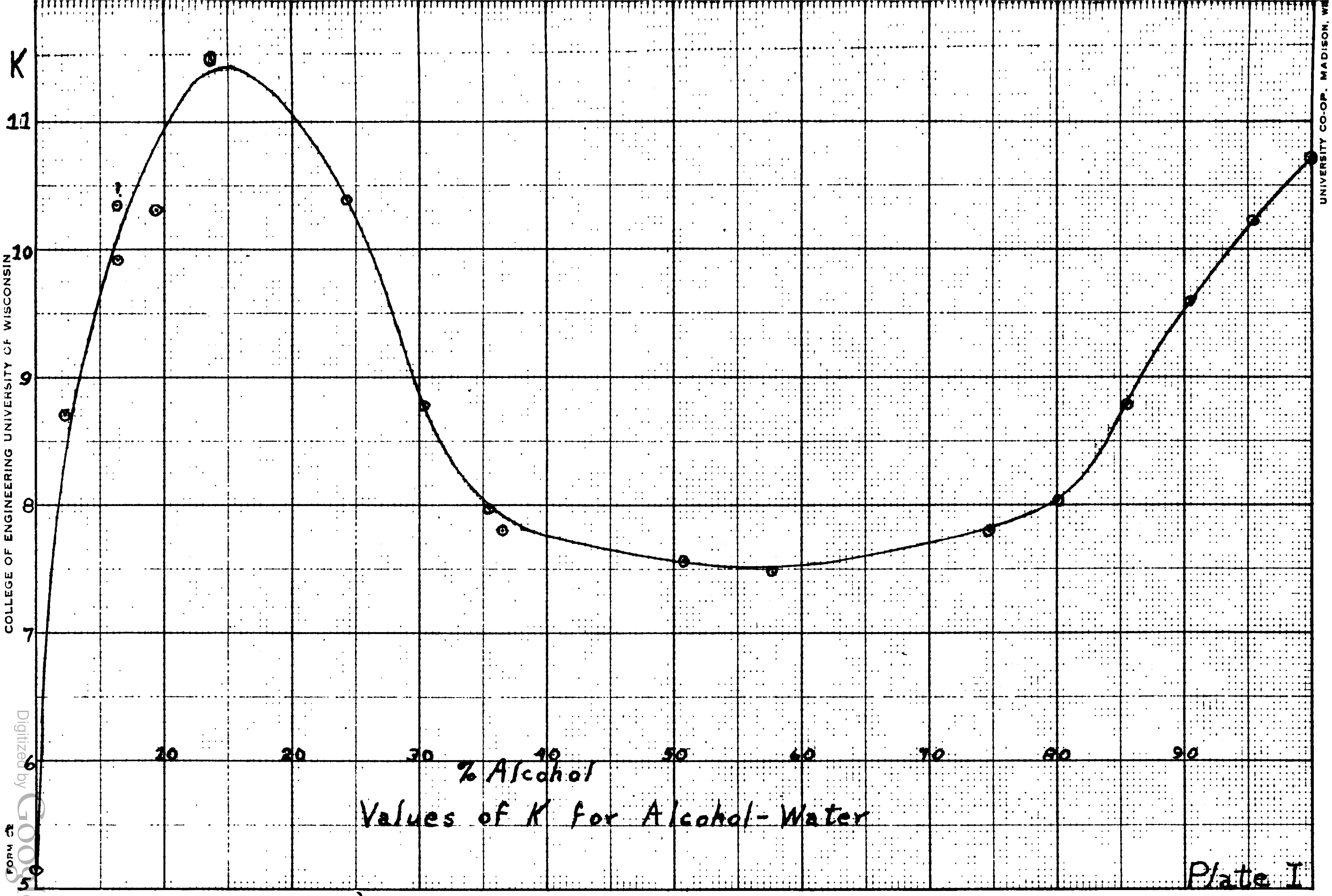
Finally, the results have shown that:

(1) An elevation-composition curve for a mixture is probably not independent of the nature of the solute used. This should be checked by further experimentation.

(2) The values of K determined for pure liquids do not agree within the limits of experimental error with those

calculated by $K = \frac{RT^2}{L}$ nor do they agree with those calculated by $K = \frac{Po - p}{\frac{dp}{dT}} \cdot \frac{M}{G}$ but in the latter case, the disagreement is probably due to inaccuracy in the existing data for $\frac{dp}{dT}$ and these calculations should be repeated as soon as better data is available for $\frac{dp}{dT}$.

The writer wishes to take this opportunity to express his thanks to Dr. J. H. Mathews for the aid and encouragement he has given in carrying out this work.



Values of K for Alcohol-Water

Plate I

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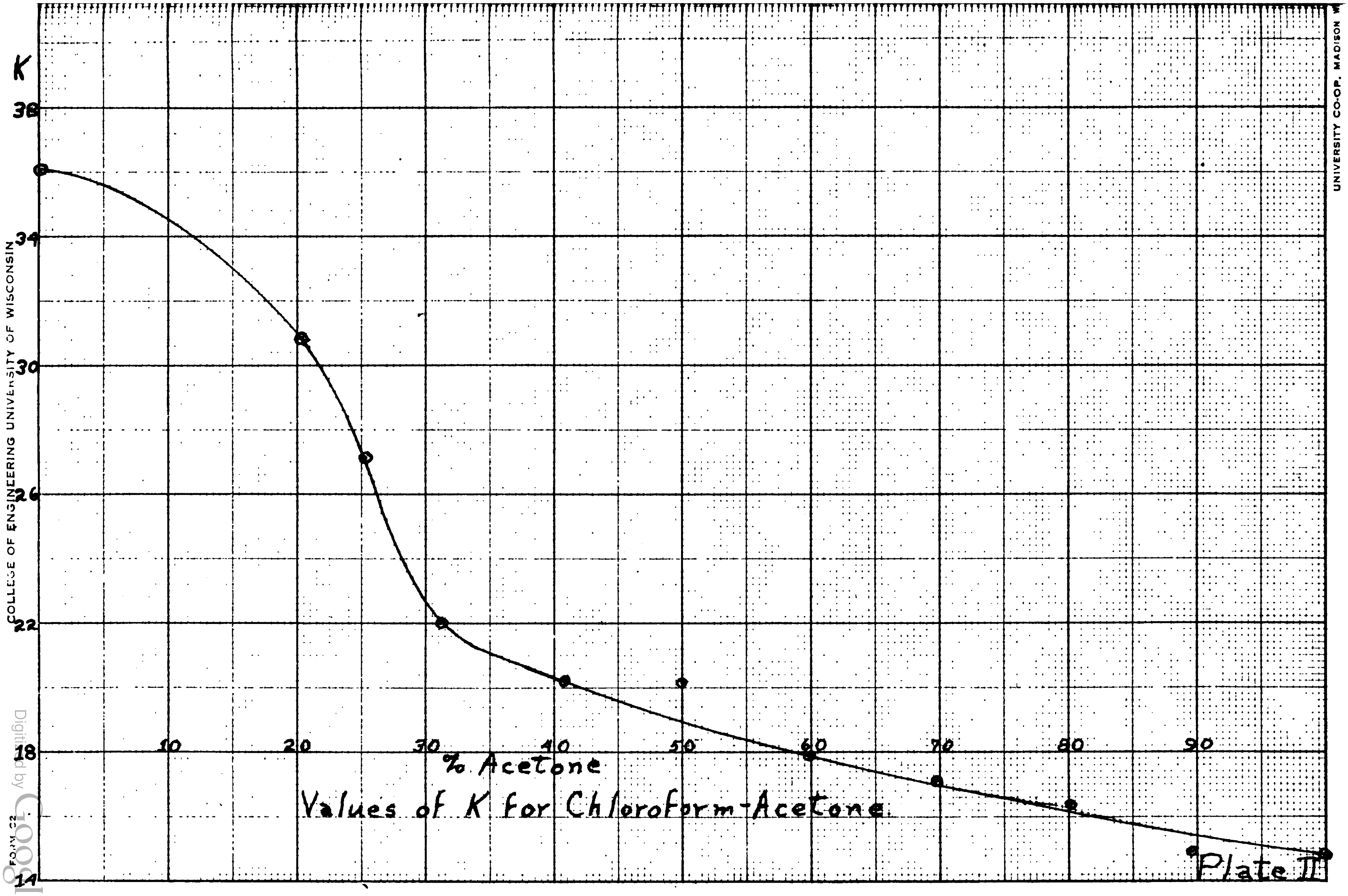
UNIVERSITY CO-OP. MADISON, WIS



Values of K for Chloroform-Acetone

Plate II

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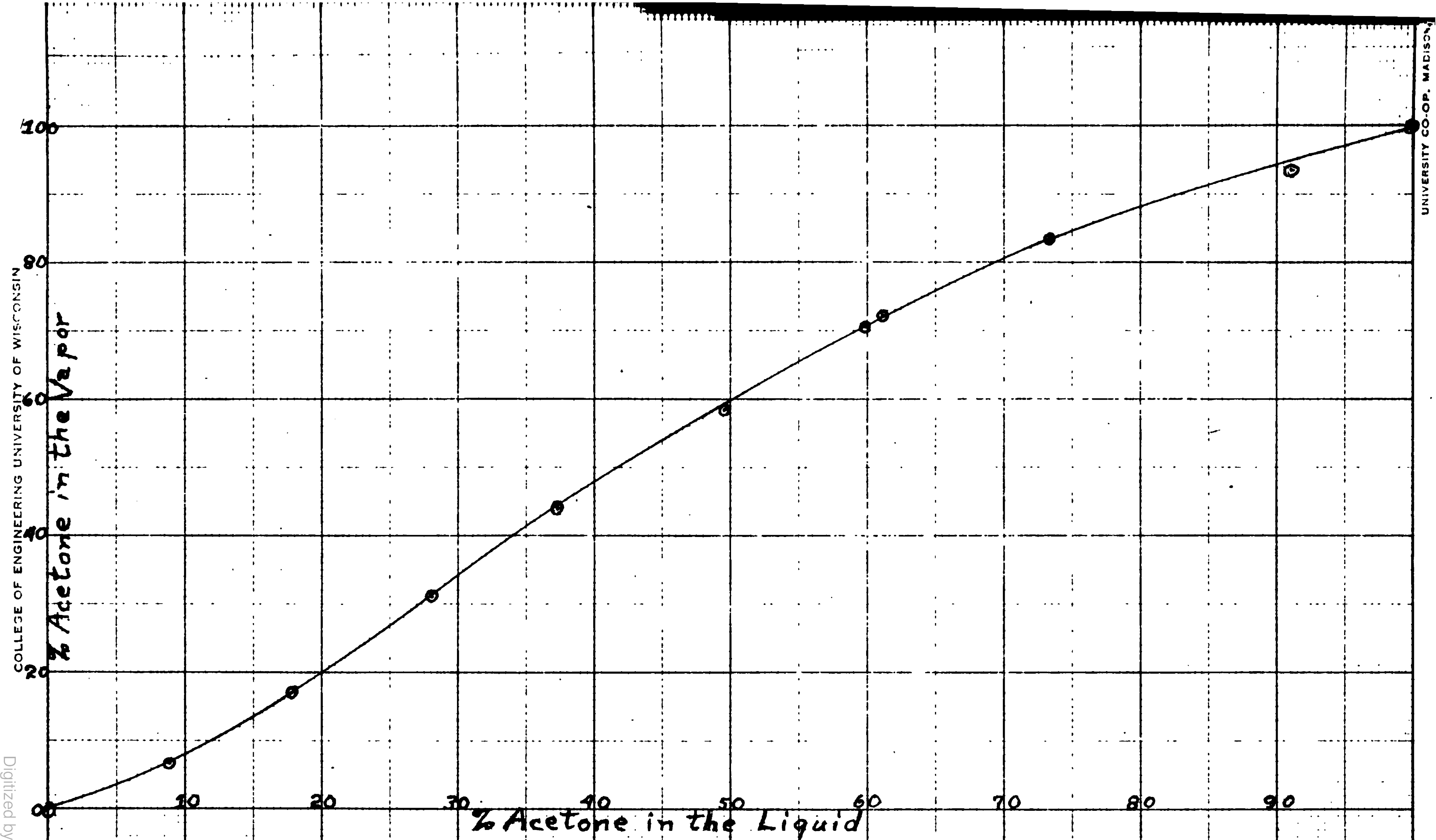
UNIVERSITY CO-OP, MADISON W

FORM 52



Vapor Compositions for Chloroform-Acetone.

Plate III

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UNIVERSITY CO-OP. MADISON

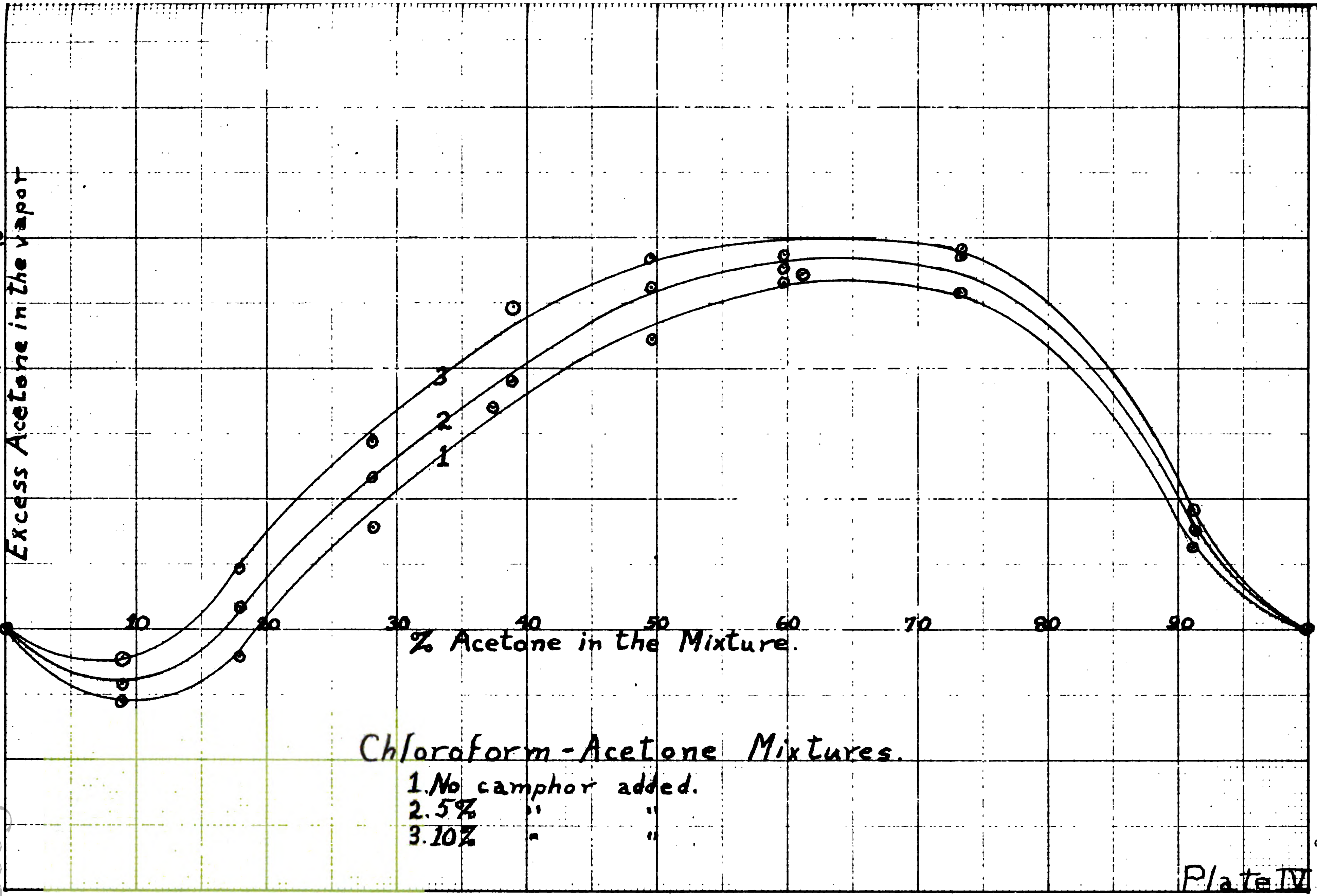

Plate IV

FORM C2

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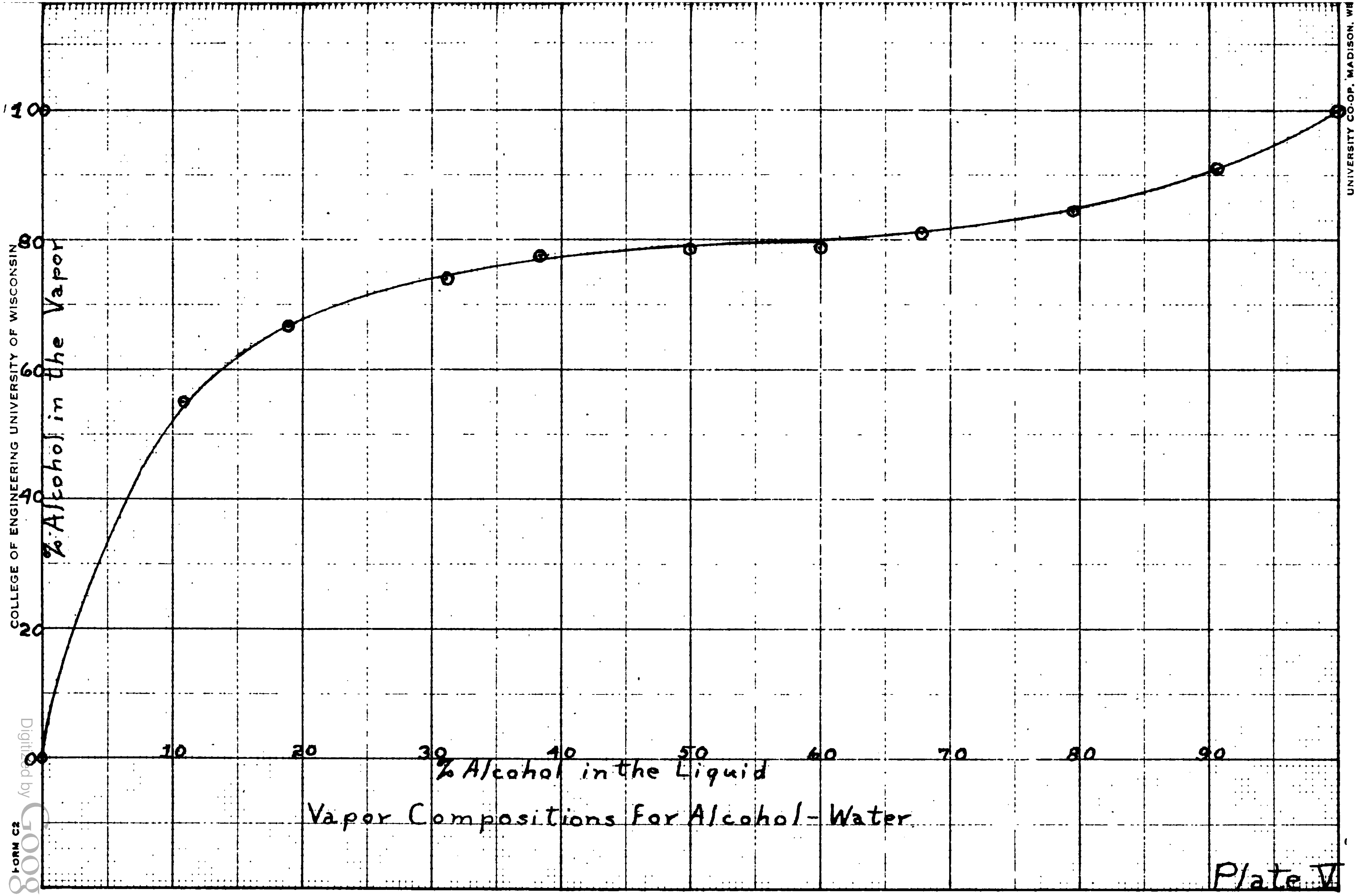

Vapor Compositions For Alcohol-Water

Plate V

FORM C2

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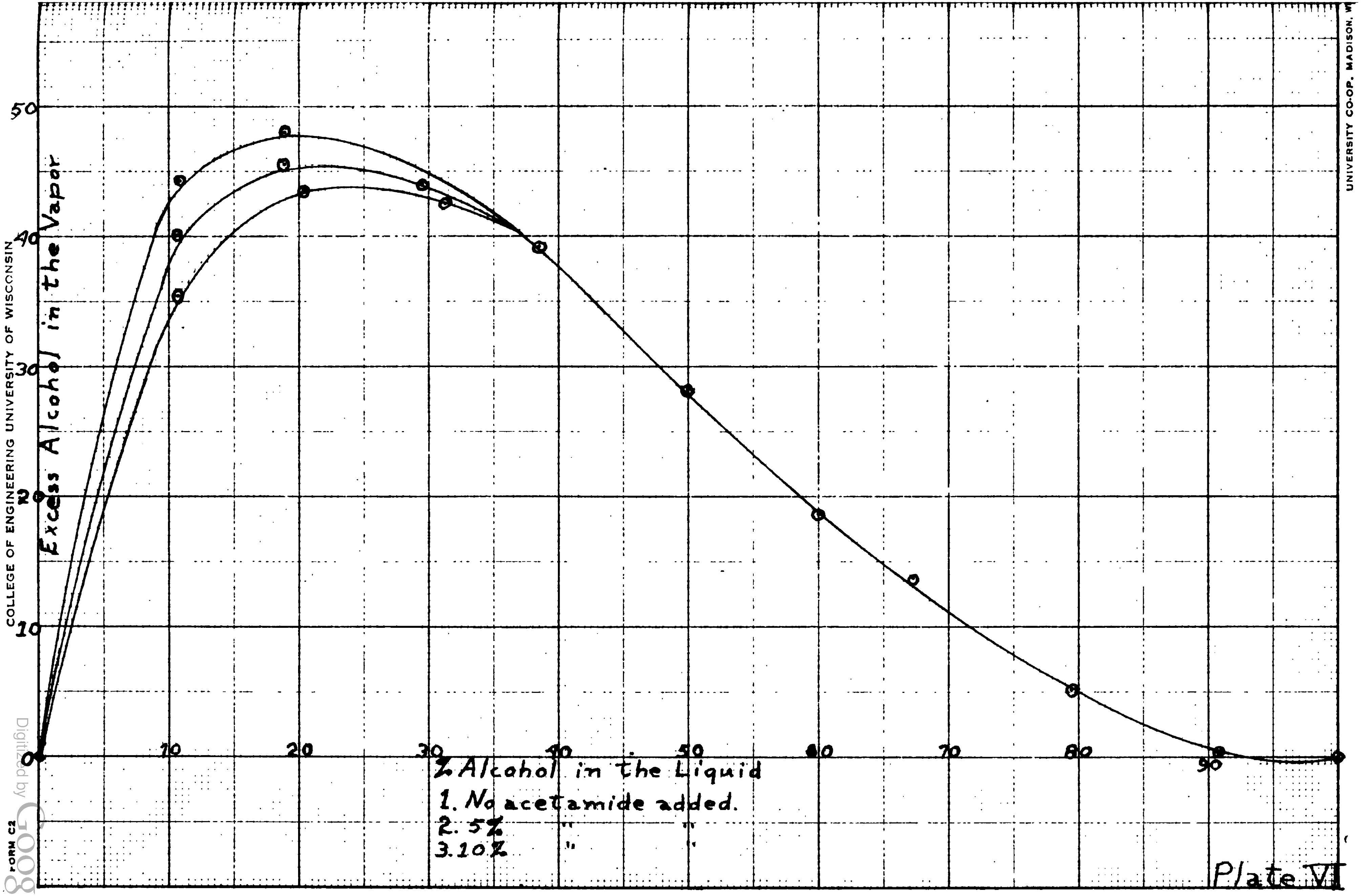

Plate VI

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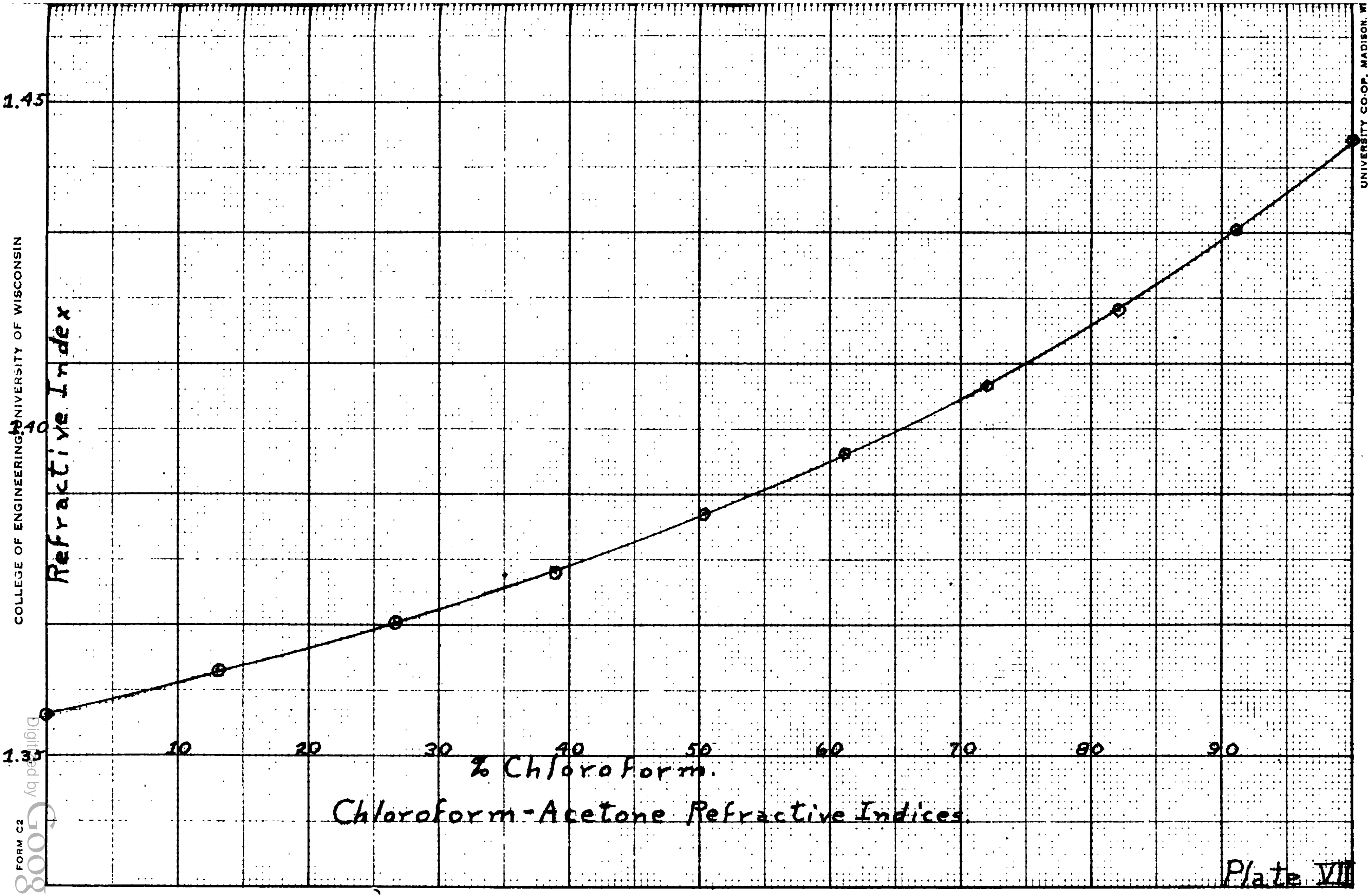
FORM C2



Chloroform-Acetone Refractive Indices.

Plate VII

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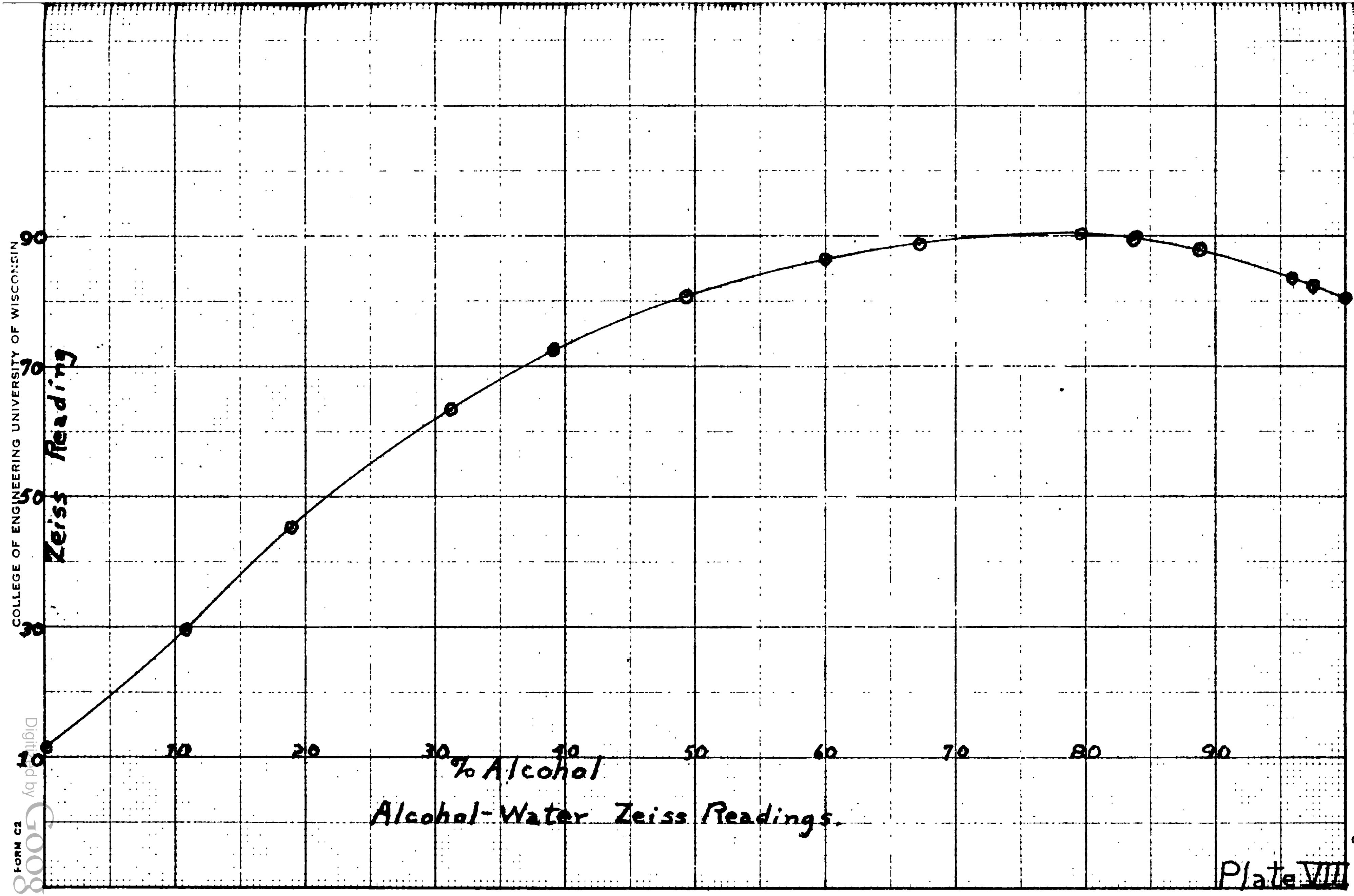
UNIVERSITY CO-OP. MADISON, WI



Alcohol-Water Zeiss Readings.

Plate VIII

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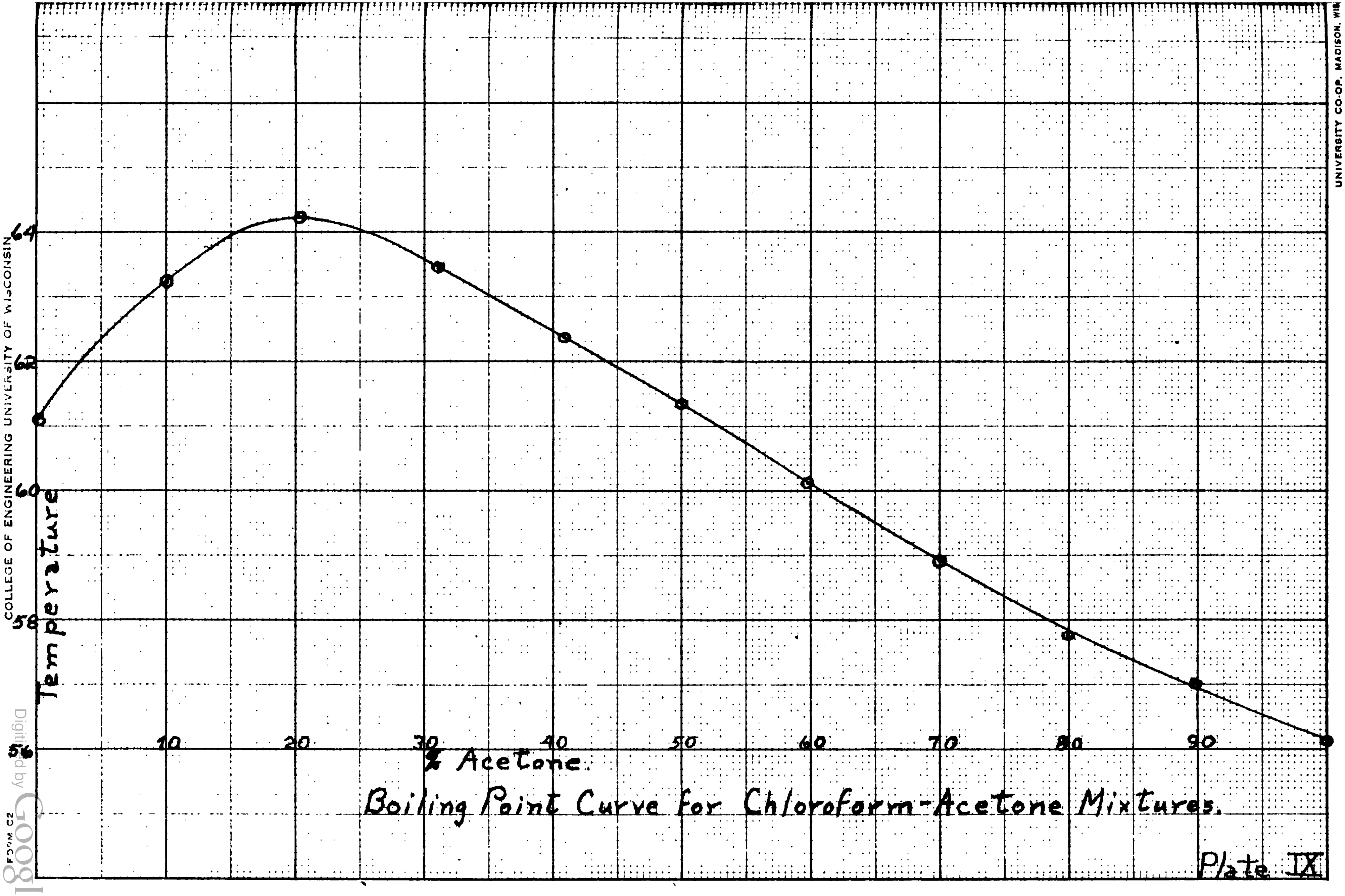

Boiling Point Curve for Chloroform-Acetone Mixtures.

Plate IX

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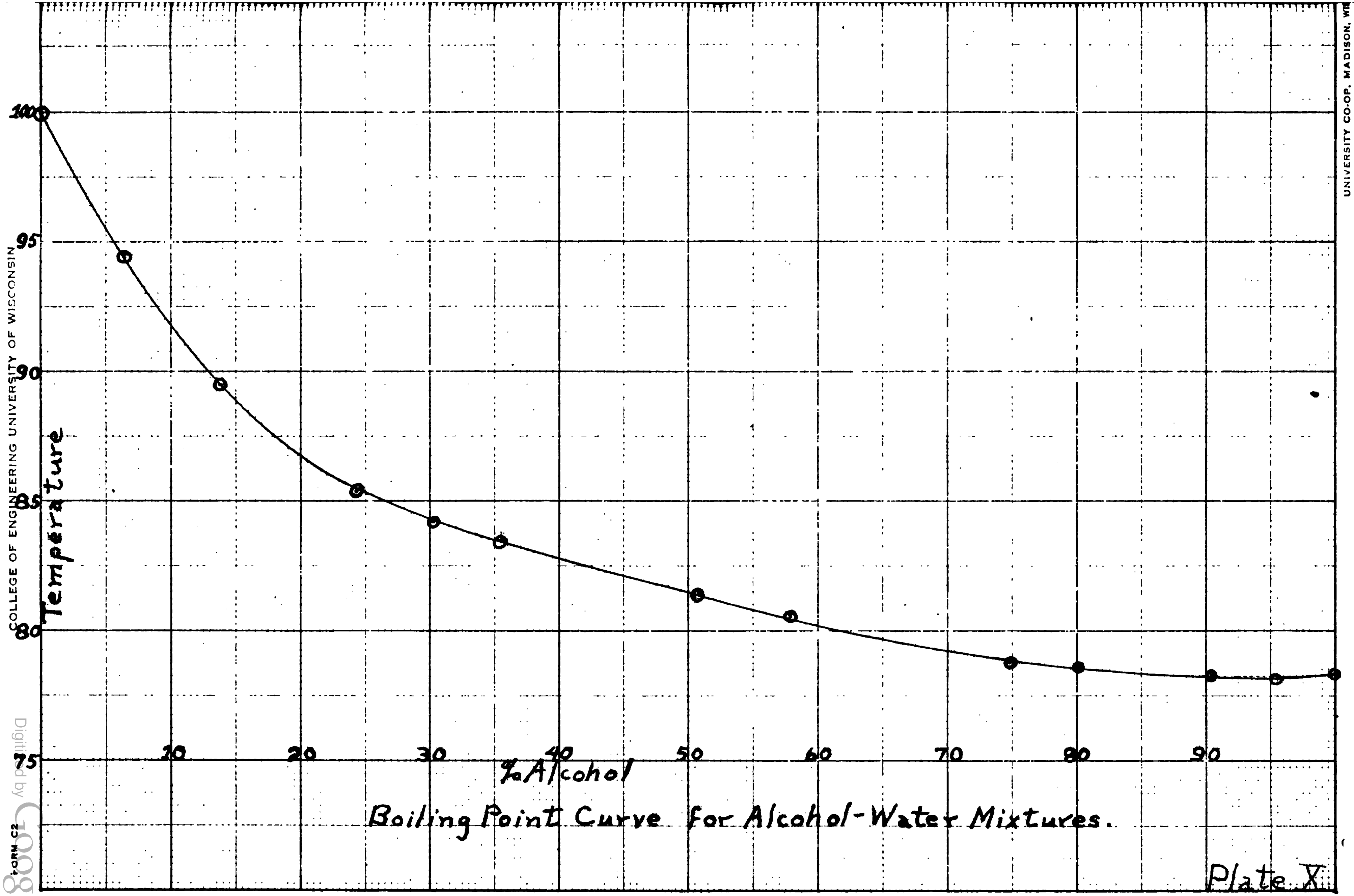
FORM C2



Boiling Point Curve for Alcohol-Water Mixtures.

Plate X

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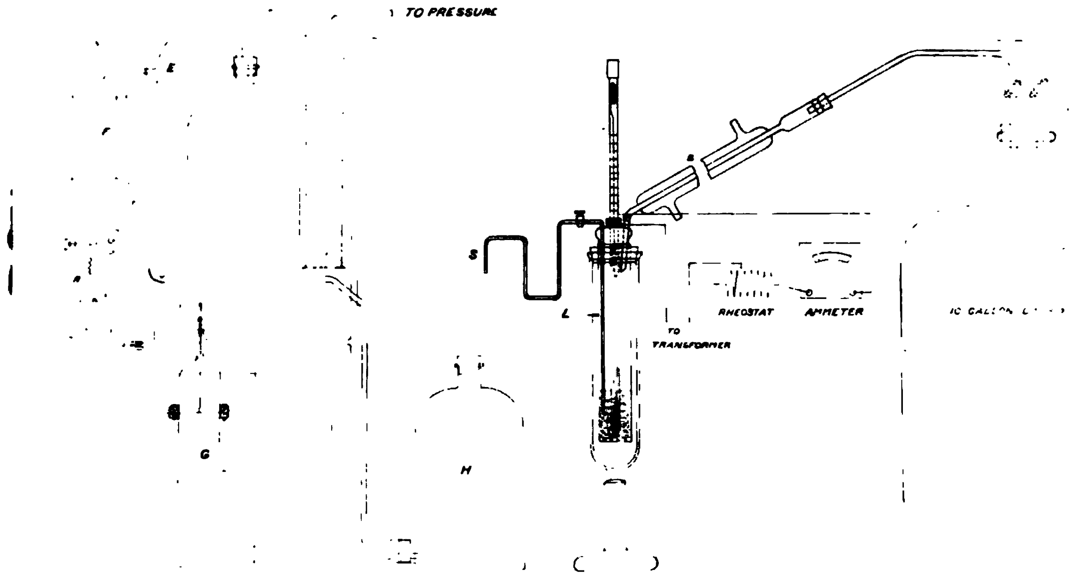
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Approved Farrington Daniels
(for J. H. Mathews)

Date Aug 3, 1921.

Approved Farrington Daniels
(for J. H. Mathews)

Date Aug 3, 1921.

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